

# THz Rotational Spectra of HBr Isotopomers in their $v = 0, 1$ States

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We have observed the pure rotational spectra of HBr isotopomers in their  $v = 0$  and  $v = 1$  states between 0.97 and 1.02 THz, i. e. the HBr  $J = 2 - 1$  and the DBr  $J = 4 - 3$  transitions, respectively. In the analysis, all presently available rotational transitions of all isotopomers have been fitted to a Dunham-type Hamiltonian to obtain the isotopically invariant parameters, including vibrational and rotational expansion coefficients for the hyperfine constants. In the analysis, the vibrational expansion coefficients of the nuclear quadrupole interaction are determined up to second order, and up to first order for the nuclear spin-rotation interaction.

## 1. Introduction

While the rotational Hamiltonian in diatomic molecules is often treated using Dunham's results in a form including correction parameters for the breakdown of the Born-Oppenheimer approximation (cf. e. g. [1]), a similar expansion for the hfs constants, as introduced by Ryzlewicz et al. [2], is not so frequently employed. However, this approach is interesting since it will improve the ratio between observed transitions and determined parameters. Diatomic molecules including hydrogen atoms provide a good test for this approach since the substitution  $H \rightarrow D$  changes the reduced mass strongly. HBr, with hyperfine structure due to both nuclei, thus serves as an interesting candidate.

Ro-vibrational spectra of HBr isotopomers have been investigated by several authors; a good overview and a thorough analysis of the isotopic dependence of Born-Oppenheimer breakdown effects is given in the work of Coxon and Hajigeorgiou [3]. Special attention to the bromine hyperfine structure is paid in a paper by Wells et al. [4], where a first estimate for the quadrupole hyperfine constants in the first excited vibrational state of  $D^{79}\text{Br}$  has been extracted from an analysis of the  $v = 1 - 0$  band.

Previous work on HBr pure rotational spectra cover the vibrational ground state of several isotopomers. Very accurate molecular beam spectra of the  $J = 1 - 0$  transition of HBr and DBr have been made by van Dijk and Dymanus [5, 6], clearly resolving the hfs patterns of both nuclei in the molecule. De Lucia et al. [7] have recorded a wider range of transitions, but with less accuracy. Far-infrared rotational spectra up to 4.5 THz have been measured by Di Lonardo et al. [8].

The sensitivity of our THz spectrometer has allowed us to measure for the first time pure rotational transitions of  $H^{79}\text{Br}$ ,  $H^{81}\text{Br}$ ,  $D^{79}\text{Br}$  and  $D^{81}\text{Br}$  in the first excited vibrational state. Ground state THz spectra of  $D^{79}\text{Br}$  and  $D^{81}\text{Br}$  have also been recorded. The analysis will show a simultaneous fit of all presently available rotational transitions for the four isotopomers.

## 2. Hamiltonian

The rotational part of the Dunham-type Hamiltonian was already discussed in our previous publications on rotational spectra of the CN and SO radicals [1, 9]. The emphasis here will lie on the isotopically invariant Dunham-type expansions of the hyperfine structure (hfs) parameters  $eQq$ ,  $C_I$  and  $d_T$ , requiring additional terms not included in those previous works. Therefore, we review it to somewhat more detail.

The dominant contribution to the hfs is caused by the nuclear electric quadrupole hfs of the Br nuclei. In the case of deuterated species, the very small quadrupole moment of the deuteron (spin  $I = 1$ ) gives also rise to an additional quadrupole hfs (for hydrogen

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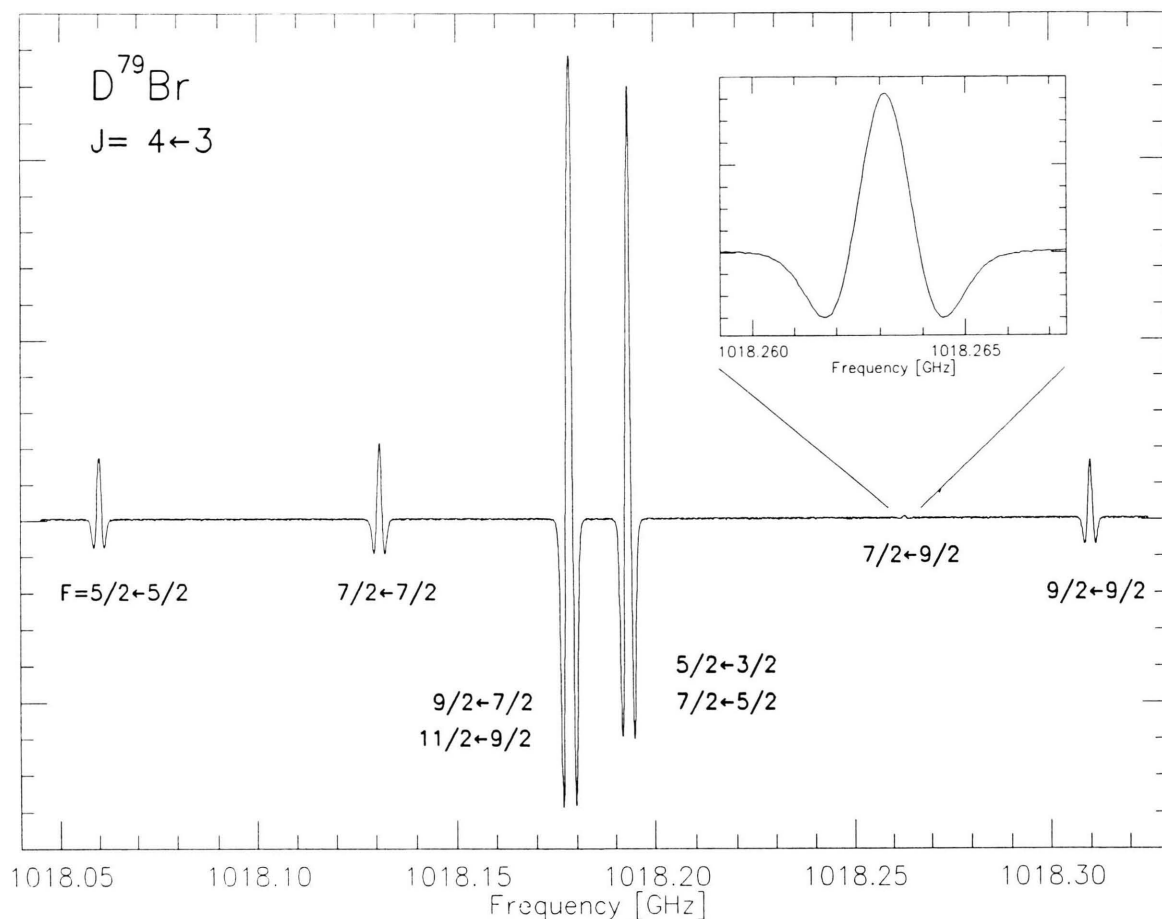


Fig. 1. 32-MHz scan showing the  $^{79}\text{Br}$  hyperfine structure of the  $J = 4 \leftarrow 3$  transition of  $\text{D}^{79}\text{Br}$  at 1.018 THz. Each individual line was measured with higher signal-to-noise-ratio than shown in the overview scan as demonstrated for the  $F = 7/2 \leftarrow 9/2$  transition.

atoms, this is not the case since its nuclear spin is  $I = 1/2$ ). Following Ryzlewicz *et al.* [2], the nuclear electric quadrupole coupling constant is expanded in a Dunham-type series as

$$eQq = Q \sum_{ij} eq_{ij} \mu^{-i/2-j} (v + 1/2)^i J^j (J + 1)^j. \quad (1)$$

A second contribution to the hyperfine structure arises from the interaction between nuclear spin and rotation of the molecular frame. It applies to all H and Br isotopes. In contrast to the electric quadrupole hfs, it is a second-order effect, theoretically treated as a perturbation by excited electronic states. As pointed out by Townes and Schawlow [10], the associated nuclear magnetic coupling parameter  $C_I$

is approximately proportional to the rotational constant  $B$ . Since  $B \propto \mu^{-1}$ , we may adopt the expansion

$$C_I = \frac{\mu_I}{\mu_N I} \sum_{ij} C_{ij} \mu^{-i/2-j-1} \left(v + \frac{1}{2}\right)^i J^j (J + 1)^j, \quad (2)$$

where the  $C_{ij}$  are isotopically invariant. This expansion is surely of approximate character; the individual result of the fit will judge whether it is applicable or not. However, in general the accuracy of determined frequencies does only permit a moderately accurate determination of the  $C_I$ , so this approximation is not expected to be required in most cases. The proportionality with  $1/I$  accounts for different nuclear spins of different isotopes as  $I = 1/2$  for H and  $I = 1$  for D. The very high resolution measurements performed

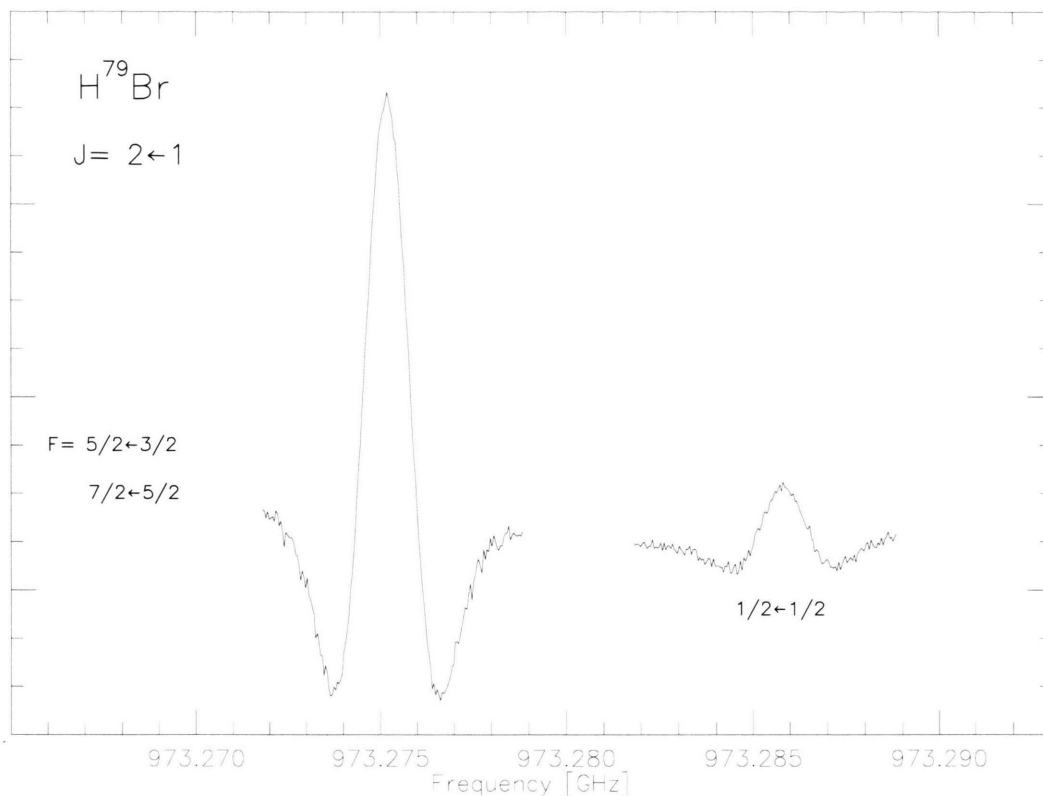


Fig. 2. The  $J = 2 \leftarrow 1$  transition of  $\text{H}^{79}\text{Br}$  in the first vibrational state. Two hfs components are shown. The peak absorption coefficient for the  $F = 1/2 \leftarrow 1/2$  lines was calculated to be about  $6.5 \cdot 10^{-8} \text{ cm}^{-1}$ .

by van Dijk and Dymanus [5, 6] on the  $J = 1 - 0$  transitions revealed a significant contribution of the magnetic interaction between the two nuclear spins, expressed by the spin-spin interaction parameter  $d_T$ ; an appropriate term is

$$d_T = \frac{\mu_{I_1} \mu_{I_2}}{\mu_N^2 I_1 I_2} \sum_{ij} d_{T,ij} \mu^{-i/2-j} \left(v + \frac{1}{2}\right)^i J^j (J+1)^j, \quad (3)$$

where the  $d_{T,ij}$  are isotopically invariant. The complete matrix elements used in the present work are given in the Appendix.

### 3. Experimental

The spectra were recorded by use of frequency and phase stabilized backward wave oscillators (BWOs) supplied by the ISTOK Research and Production Co. (Fryazino, Moscow region). For technical details the reader is referred to [11] and [12].

Briefly, the output of the high frequency BWO (OB-82, min. power 1 mW) is locked to the harmonics of a 78- to 118-GHz synthesizer, supplied by the KVARZ Co., Nizhny Novgorod, Russia. The synthesizer and the generated intermediate frequency signal are locked to a rubidium frequency standard. After passing the 4.4 meter absorption cell, the radiation is detected by a magnetically tuned InSb hot electron bolometer (QMC, U.K.), which provides enhanced sensitivity between 1 and 2 THz.

As sample spectra, Fig. 1 presents a full scan of the  $J = 4 - 3$  ( $v = 0$ ) transition of  $\text{D}^{79}\text{Br}$  at 1018 GHz, and Fig. 2 shows two lines from the hyperfine pattern of the  $J = 2 - 1$  ( $v = 1$ ) transition of  $\text{H}^{79}\text{Br}$  at 973 GHz.

### 4. Analysis and Discussion

The newly observed transitions (Table 1) have been subjected to a global fit together with frequencies reported by Dijk and Dymanus [5, 6], Di Lonardo

Table 1. Rotational transitions/MHz of HBr isotopomers measured in the present study, together with estimates of their experimental uncertainties and *o-c* values obtained from the global fit (see Table 2).

$J'$	$F'$	$-J''$	$F''$	$v$	Frequency	$\Delta\nu^a$	<i>o-c</i> <sup>b</sup>
<b>H<sup>79</sup>Br</b>							
2	0.5	1	1.5	1	973040.390	0.100	-0.041
2	1.5	1	1.5	1	973176.992	0.030	0.013
2	2.5	1	1.5	1	973275.155	0.030	0.021
2	3.5	1	2.5	1	973275.155	0.030	0.021
2	0.5	1	0.5	1	973285.793	0.050	-0.065
2	2.5	1	2.5	1	973410.231	0.050	-0.011
2	1.5	1	0.5	1	973422.384	0.050	-0.023
<b>H<sup>81</sup>Br</b>							
2	0.5	1	1.5	1	972784.146	0.100	-0.103
2	1.5	1	1.5	1	972898.450	0.050	0.025
2	2.5	1	1.5	1	972980.690	0.030	0.029 <sup>c</sup>
2	3.5	1	2.5	1	972980.690	0.030	0.029 <sup>c</sup>
2	0.5	1	0.5	1	972989.320	0.050	-0.077
2	1.5	1	2.5	1	973011.250	0.200	-0.007
2	2.5	1	2.5	1	973093.293	0.030	0.002
2	1.5	1	0.5	1	973103.639	0.150	0.065
<b>D<sup>79</sup>Br</b>							
4	2.5	3	3.5	0	1017997.780	0.030	-0.015
4	2.5	3	2.5	0	1018060.208	0.030	-0.010
4	3.5	3	3.5	0	1018131.035	0.030	-0.000
4	4.5	3	3.5	0	1018178.288	0.020	0.003 <sup>c</sup>
4	5.5	3	4.5	0	1018178.288	0.020	0.003 <sup>c</sup>
4	2.5	3	1.5	0	1018193.381	0.020	-0.001 <sup>c</sup>
4	3.5	3	2.5	0	1018193.381	0.020	-0.001 <sup>c</sup>
4	3.5	3	4.5	0	1018263.081	0.030	0.009
4	4.5	3	4.5	0	1018310.267	0.030	0.008
4	2.5	3	2.5	1	997976.908	0.100	-0.114
4	3.5	3	3.5	1	998048.949	0.100	0.001
4	4.5	3	3.5	1	998096.964	0.030	0.002 <sup>c</sup>
4	5.5	3	4.5	1	998096.964	0.030	0.002 <sup>c</sup>
4	2.5	3	1.5	1	998112.290	0.030	0.005 <sup>c</sup>
4	3.5	3	2.5	1	998112.290	0.030	0.005 <sup>c</sup>
4	4.5	3	4.5	1	998230.992	0.100	0.017
<b>D<sup>81</sup>Br</b>							
4	2.5	3	3.5	0	1017405.750	0.030	-0.006
4	2.5	3	2.5	0	1017458.017	0.030	-0.012
4	3.5	3	3.5	0	1017517.184	0.030	-0.000
4	4.5	3	3.5	0	1017556.839	0.020	0.003 <sup>c</sup>
4	5.5	3	4.5	0	1017556.839	0.020	0.003 <sup>c</sup>
4	2.5	3	1.5	0	1017569.377	0.020	-0.002 <sup>c</sup>
4	3.5	3	2.5	0	1017569.377	0.020	-0.002 <sup>c</sup>
4	3.5	3	4.5	0	1017627.337	0.030	0.012
4	4.5	3	4.5	0	1017666.912	0.030	0.007
4	2.5	3	2.5	1	997393.588	0.100	-0.045
4	3.5	3	3.5	1	997453.711	0.100	-0.003
4	4.5	3	3.5	1	997494.013	0.030	0.000 <sup>c</sup>
4	5.5	3	4.5	1	997494.013	0.030	0.000 <sup>c</sup>
4	2.5	3	1.5	1	997506.738	0.030	-0.003 <sup>c</sup>
4	3.5	3	2.5	1	997506.738	0.030	-0.003 <sup>c</sup>
4	4.5	3	4.5	1	997605.872	0.100	0.096

<sup>a</sup> Estimated experimental uncertainty; <sup>b</sup> Observed-minus-calculated value; <sup>c</sup> Calculated frequency taken as sum of hfs components – see text.

Table 2. Isotopically invariant parameters obtained in the global fit and constrained values from literature. The hfs expansion parameters are compared with results derived from previous studies.

Parameter	Here <sup>a</sup>	Previous	Unit
fitted:			
$U_{01}^c$	252604.189 (13)		MHz amu
$U_{01}^{\text{Br}}$	0.267 (4)		MHz amu
$U_{01}^{\text{H}}$	-13.123 (6)		MHz amu
$U_{11}$	-6927.27 (3)		MHz amu <sup>3/2</sup>
$U_{21}$	12.004 (14)		MHz amu <sup>2</sup>
$U_{02}$	-10.2605 (4)		MHz amu <sup>2</sup>
$U_{12}$	0.0784 (9)		MHz amu <sup>5/2</sup>
$U_{03} \times 10^6$	238 (2)		MHz amu <sup>3</sup>
$U_{04} \times 10^9$	-55 (16)		MHz amu <sup>4</sup>
$\epsilon q_{00} \times Q(^{81}\text{Br})$	439.938 (14)	439.8 (3) <sup>b</sup>	MHz
$\epsilon q_{10} \times Q(^{81}\text{Br})$	9.15 (6)	9.68 (3) <sup>b</sup>	MHz amu <sup>1/2</sup>
$\epsilon q_{20} \times Q(^{81}\text{Br})$	0.40 (6)		MHz amu
$\epsilon q_{01} \times Q(^{81}\text{Br})$	0.0268 (13)	0.0268 (18) <sup>c</sup>	MHz
$C_{00}(\text{Br})$	0.1989 (9)		MHz
$C_{10}(\text{Br})$	0.0143 (19)		MHz amu <sup>1/2</sup>
$\epsilon q_{00} \times Q(\text{D})$	0.1469 (13)	0.1469 (19) <sup>d</sup>	MHz
$C_{00}(\text{H})$	-0.00735 (4)	-0.00739 (6) <sup>e</sup>	MHz
$d_{T,00}(\text{Br}, \text{H})$	0.001286 (19)	0.001280 (27) <sup>e</sup>	MHz
fixed: <sup>f</sup>			
$m(\text{H})$	1.007825035		amu
$m(\text{D})$	2.014101779		amu
$m(^{79}\text{Br})$	78.9183361		amu
$m(^{81}\text{Br})$	80.916289		amu
$Q(^{79}\text{Br})/Q(^{81}\text{Br})$	1.197052		
$\mu_I/\mu_N(\text{H})$	2.7928456		
$\mu_I/\mu_N(\text{D})$	0.8574376		
$\mu_I/\mu_N(^{79}\text{Br})$	2.106399		
$\mu_I/\mu_N(^{81}\text{Br})$	2.270560		

<sup>a</sup> Values in brackets: 1 $\sigma$ ; <sup>b</sup> [6]; <sup>c</sup> Calculated from H<sup>79</sup>Br  $v = 0$  value ([8]); <sup>d</sup> D<sup>79</sup>Br  $v = 0$  value ([6]); <sup>e</sup> Calculated from H<sup>79</sup>Br  $v = 0$  value ([5]); <sup>f</sup> Values taken from [15] except for  $Q(^{79}\text{Br})/Q(^{81}\text{Br})$ , taken from [14].

et al. [8] and De Lucia et al. [7]. Of the last mentioned, the two DBr  $J = 3 - 2$  lines were not included in the fit for they were estimated to have large uncertainties compared to our new 4 - 3 data. The total number of included line positions amounted to 152. Following Rudolph [13], non-resolved hyperfine splittings have been calculated as sum of their intensity-weighted average. The quality of the global fit is excellent, since all data taken from literature have been fitted to

the same quality as given in their original references, where each state of each isotopomer had been fitted separately. The molecular constants obtained by this procedure are shown in Table 2. The o-c values from Table 1 show that the new frequencies are also very well reproduced, strong lines having o-c values better than 10 kHz, corresponding to an uncertainty of  $10^{-8}$  in the frequencies. Even the faintest measured components of the HBr  $v = 1$  states do not deviate by more than 100 kHz from their calculated values. This underlines the potential of the combination of sensitivity and resolution achieved with the Cologne THz spectrometer.

For the global fit in the method described above, values for the nuclear electric quadrupole moments have to be taken from the literature. The absolute values of the nuclear quadrupole moments are not known to the required accuracy; nevertheless, their ratio for the bromine nuclei  $Q(^{79}\text{Br})/Q(^{81}\text{Br})$  is very accurately known [14]. We have fixed the ratio at this value and determined  $Q(^{81}\text{Br})$  in the fit. Accurate nuclear magnetic moments  $\mu_I/\mu_N$  as well as atomic masses were taken as compiled by the IUPAC [15].

The successful simultaneous fitting reveals the ability of the Dunham-type approach also for the hyperfine constants. Only nine hyperfine constants were needed in the global fit, whereas e.g. the high-resolution data for the  $v = 0$  state of  $\text{D}^{79}\text{Br}$  only, already require five hyperfine constants. Although the present measurements report the first pure rotational spectra in the  $v = 1$  states, the first order vibrational dependence of the  $eQq$  constants for the bromine nuclei had already been noticed earlier. Dijk and Dymanus [6] have determined it from the isotopic shifts in the bromine  $eQq$  by comparison of HBr to DBr. Our global fit including the new  $v = 1$  transitions also yields the second order vibrational dependence coefficient  $eQq_{20}$  to be of significance. The equilibrium value  $eQq_{00}$  of Dijk and Dymanus agrees well with ours, whereas there is a small difference in the first vibrational expansion parameter  $eQq_{10}$  since they had not determined  $eQq_{20}$ .

Concerning the nuclear spin-rotation interaction of the bromine nuclei, the vibrational dependence could be determined for the first time in the present work. It should be mentioned that the vibrational correction  $C_{10}$  is positive, whereas the corresponding parameter  $U_{11}$ , related to the rotational constant  $B$ , is negative: while the proportionality of  $C_I$  and  $B$  is well obeyed for isotopic substitution within the same vibrational

Table 3. HBr hfs constants/MHz derived from the fit shown in Table 2, in comparison to values reported by other authors.

		Here <sup>a</sup>	[8]	[5, 6]	[4]
$\text{H}^{79}\text{Br}$	$eQq_J$	0.0322 (16)	0.03229 (212)		
	$v = 0$				
	$eQq$	532.240 (3)	532.23977 (569)	532.3041 <sup>b</sup> (8)	
	$C_I$	0.29075 (6)	0.289091 (396)	0.29083 (8)	
	$v = 1$				
	$eQq$	544.19 (8)			
$\text{H}^{81}\text{Br}$	$C_I$	0.311 (3)			
	$eQq_J$	0.0269 (13)	0.02530 (336)		
	$v = 0$				
	$eQq$	444.625 (3)	444.62872 (901)	444.6793 <sup>b</sup> (8)	
	$C_I$	0.31331 (6)	0.311971 (631)	0.31325 (8)	
	$v = 1$				
$\text{D}^{79}\text{Br}$	$eQq$	454.60 (7)			
	$C_I$	0.335 (3)			
	$eQq_J$	0.0163 (8)			
	$v = 0$				
	$eQq$	530.598 (3)		530.6315 <sup>b</sup> (21)	
	$C_I$	0.14584 (19)		0.14582 (24)	
$\text{D}^{81}\text{Br}$	$v = 1$				
	$eQq$	538.90 (3)			557.2 (100)
	$C_I$	0.1531 (8)			0.146 <sup>c</sup>
	$eQq_J$	0.0136 (7)			
	$v = 0$				
	$eQq$	443.253 (2)		443.2799 <sup>b</sup> (21)	
$\text{D}^{79}\text{Br}$	$C_I$	0.1571 (2)		0.15726 (24)	
	$v = 1$				
	$eQq$	450.19 (2)			
	$C_I$	0.165 (8)			

<sup>a</sup> Values in brackets:  $1\sigma$ ; <sup>b</sup>  $eQq + 2eQq_J$  – see text; <sup>c</sup> Fixed.

state, it does not hold for a change of the vibrational quantum number: by an increase of  $v$ , also  $C_{I,v}$  increases while  $B_v$  decreases. Furthermore, the relative vibrational dependence of  $C_I$  is larger than for the rotational constant.

Table 3 shows bromine hyperfine constants for the individual states involved, derived from our global fit, in comparison to the most accurate previous values. All  $v = 0$  constants previously reported by Di Lonardo et al. [8] and van Dijk and Dymanus [5, 6] are reproduced within  $1\sigma$  (the  $eQq$ 's in [5, 6] correspond to  $eQq + 2eQq_J$  for being derived from the  $J = 1-0$  transitions only). A value for  $eQq(\text{D}^{79}\text{Br})$  in the  $v = 1$  state, although with large error bars, was derived from a study of the  $v = 1 - 0$  band [4]. Their values do not agree within their uncertainties with our more accurate values, and also contradict the vibrational dependence already obtained by van Dijk and Dymanus [6].

The hydrogen hyperfine structure parameters, as well as the magnetic spin-spin interaction parameter  $d_T$  between the bromine and hydrogen nuclei, agree perfectly with the constants in [5, 6], and here therefore, they are not tabulated for each state separately.

## 5. Conclusion

The sensitivity and resolution of the Cologne THz spectrometer has enabled us to observe rotational

spectra of HBr isotopomers for the first time. In the analysis, it is shown that a Dunham-type expansion including all relevant hyperfine parameters is very suitable to reproduce all hitherto observed rotational spectra of the species. The vibrational dependence of the electric quadrupole and magnetic spin-rotation hyperfine structure has been precisely determined. In particular, the nuclear spin-rotation constants increase with increasing  $v$  and thus do not show a proportionality with the rotational constant  $B$ , whereas such a

proportionality holds very well under isotopic substitution.

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## Appendix

The matrix elements employed in the present study are as follows:

$$\langle J' I_1 F'_1 I_2 F | H | J I_1 F_1 I_2 F \rangle = \quad (A1)$$

$$\begin{aligned} & \delta_{JJ'} \delta_{F_1 F'_1} \sum_{ij} U_{ij} \mu^{-i/2-j} (v+1/2)^i J^j (J+1)^j \\ & + \frac{1}{4} \delta_{F_1 F'_1} e q Q_1 (-1)^{I_1+J'+F_1+2+J'} \begin{Bmatrix} F_1 & J' & I_1 \\ 2 & I_1 & J \end{Bmatrix} \begin{pmatrix} J' & 2 & J \\ 0 & 0 & 0 \end{pmatrix} \sqrt{(2J'+1)(2J+1) \frac{(I_1+1)(2I_1+1)(2I_1+3)}{I_1(2I_1-1)}} \\ & + \delta_{F_1 F'_1} \delta_{JJ'} C_{I_1} (-1)^{I_1+J'+F_1+1} \begin{Bmatrix} F_1 & J' & I_1 \\ 1 & I_1 & J \end{Bmatrix} \sqrt{J(J+1)(2J+1)I_1(I_1+1)(2I_1+1)} \\ & + \frac{1}{4} e q Q_2 (-1)^{I_2+F'_1+F+J+I_1+F'_1+4+J'} \begin{Bmatrix} F & F'_1 & I_2 \\ 2 & I_2 & F_1 \end{Bmatrix} \begin{Bmatrix} J' & F'_1 & I_1 \\ F_1 & J & 2 \end{Bmatrix} \begin{pmatrix} J' & 2 & J \\ 0 & 0 & 0 \end{pmatrix} \\ & \quad \times \sqrt{(2F'_1+1)(2F_1+1)(2J'+1)(2J+1) \frac{(I_2+1)(2I_2+1)(2I_2+3)}{I_2(2I_2-1)}} \\ & + \delta_{JJ'} C_{I_2} (-1)^{I_2+F'_1+F+J+I_1+J+F'_1+2} \begin{Bmatrix} F & F'_1 & I_2 \\ 1 & I_2 & F_1 \end{Bmatrix} \begin{Bmatrix} J' & F'_1 & I_1 \\ F_1 & J & 1 \end{Bmatrix} \\ & \quad \times \sqrt{(2F'_1+1)(2F_1+1)J(J+1)(2J+1)I_2(I_2+1)(2I_2+1)} \\ & + \sqrt{30} d_T (-1)^{I_2+F'_1+F+J'+2} \begin{Bmatrix} F & F'_1 & I_2 \\ 1 & I_2 & F_1 \end{Bmatrix} \begin{Bmatrix} I_1 & I_1 & 1 \\ J' & J & 2 \\ F'_1 & F_1 & 1 \end{Bmatrix} \begin{pmatrix} J' & 2 & J \\ 0 & 0 & 0 \end{pmatrix} \\ & \quad \times \sqrt{I_2(I_2+1)(2I_2+1)I_1(I_1+1)(2I_1+1)(2F_1+1)(2F'_1+1)(2J+1)(2J'+1)}. \end{aligned}$$

To account for the breakdown of the Born-Oppenheimer approximation, in the first term  $U_{01}$  is substituted by [16]

$$U_{01} = U_{01}^e + U_{01}^A \left(1 - \frac{M_A^0}{M_A}\right) + U_{01}^B \left(1 - \frac{M_B^0}{M_B}\right), \quad (A2)$$

where A and B refer to the isotopes A and B of the nuclei 1 and 2, respectively.  $M_A^0$  and  $M_B^0$  are the atomic masses in the reference isotopomer, here  $\text{H}^{79}\text{Br}$ .

For the Dunham-type expansion of hyperfine constants, (1) - (3), have been used.



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